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(71) Applicant
United Kingdom Atomic Energy Authority

(Incorporated in the United Kingdom)

11 Charles II Street, London, SW1Y 4QP,
United Kingdom

(72) Inventors
Christopher James Bedell
Geoffrey Dearnaley

(74) Agent and/or Address for Service
Paul Austin Wood
Patents Branch, Building 329, Harwell Laboratory,
Oxfordshire, United Kingdom

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(54) Surface protection of titanium

(57) A method of protecting artefacts made of titanium or its alloys against the effects of a reactive gaseous environment, comprising forming upon the artefact to be protected a protective coating including an outer layer made of a material which either does not react with the gaseous environment or forms a passivating compound there with and an inner barrier layer such as to prevent interdiffusion between the outer layer and the artefact. The outer layer may be chromium, chromium/nitrogen, nickel-chromium alloy, silicon oxide, silicon, boron or a noble metal such as rutherium or platinum. The inner barrier layer may be of silicon nitride. The layers may be deposited by a vacuum deposition process which is a combination of electron beam evaporation and ion bombardment. A further layer of a noble metal such as rutherium or platinum may be applied as further protection. The coated product finds special application as a compressor blade for a gas turbine aero engine.

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Vap depos (EB or IB)

[Drawings refered to in this refrence but none present with copy as found in EAST.]

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Surface Protection of Titanium

The present invention relates to the protection of titanium - containing artefacts against the effects of reactive gaseous environments and more particularly to the protection of titanium gas turbine compressor or blades against the effects of oxygen or hydrogen.

Developments in titanium alloy metallurgy have provided materials which have the strength and resistance to both fatigue and creep to enable them to be used for the compressor blades of gas turbine aeroengines at operating temperatures of more than 600°C. However, at temperatures greater than 500°C all titanium alloys are susceptible to rapid oxidation during which oxygen migrates inwards to significant depths. The presence of even a few atomic per cent of oxygen will cause high-strength titanium alloys to become brittle. This happens because of the stabilisation of the alpha-phase of titanium in the alpha-beta mixed phase structure which exists in titanium alloys. It is known also that hydogen, diffusing into titanium alloys following a surface chemical reaction, also has an embrittling effect upon such alloys.

It is known that the high temperature oxidation resistance of titanium and its alloys can be improved by means of surface coatings of other metals, for example, US Patent Specification 4,181,590 discloses a technique in which noble metal coatings are formed on titanium alloy artefacts by means of ion plating. Also, in "Ion Implantation" 729-738 Vol 8 (1973), one of the present inventors, with other co-authors, discusses corrosion studies in ion implanted metals and also the reduction of the high temperature oxidation of titanium. Among the metals with useful properties for this purpose disclosed are calcium, europium, cerium, yttrium, zinc, aluminium, nickel and bismuth. However, in practice, although the oxidation resistance of titanium may be improved by such

metals, ion implantation of them has not been shown to provide worthwhile improvements in the mechanical performance of treated titanium artefacts.

According to the present invention there is provided an artefact made of titanium or a titanium alloy having upon a surface a protective coating comprising an outer layer which is such as not to react with a reactive environment against which the artefact is to be protected or to form a passivating compound therewith and an inner barrier layer such as to prevent interdiffusion between the outer layer and the artefact.

Also according to the present invention there is provided a method of protecting artefacts made of titanium or a titanium alloy against the effects of a reactive gaseous environment, comprising forming upon the artefact to be protected a protective coating including an outer layer made of a material which either does not react with the gaseous environment or forms a passivating compound there with and an inner barrier layer such as to prevent interdiffusion between the outer layer and the artefact.

The protective coating may also include an outermost erosion resistant layer. Preferably the outer layer is made of chromium; nickel 20% chromium alloy; silicon oxide; silicon or boron and the inner barrier layer is made of silicon nitride.

Preferably, also, the barrier layer is deposited by a technique which does not raise the temperature of the surface of the titanium artefact above a temperature at which appreciable oxidation can occur. A suitable technique is that known as ion-assisted coating in which the surface of the artefact is bombarded with appropriate ions having energies in the range of 10-1000 eV. The outer layer can be deposited in the same way.

In this technique, coating atoms evaporated from a heated source and ions, generally a gaseous species, from a suitable ion source are directed simultaneously in vacuum towards the object to be coated. The resulting coating is extremely well bonded to the substrate material due to the action of energetic ions in stimulating both intermixing and strong interatomic bond formation across the critical interface region between the coating and the substrate, or subsequently between the layers of a multi-layered coating.

The invention will now be described, by way of example, with reference to the accompanying drawing which illustrates the stages of a process embodying the invention.

Referring to the drawings, a substrate 1 made of titanium alloy 625 was exposed to a beam 2 of silicon atoms which were evaporated from an electrically heated source (not shown). The silicon atom source was such that the silicon atoms were deposited at a rate between 1-10A per second. The rate of deposition of the silicon atoms was monitored and used to control the flux of a beam 3 of ions from a nitrogen ion source, agains not shown, such that a coating 4 of silicon nitride having the composition Si_3N_4 was formed on the substrate 1. The energy of the nitrogen ions was 500 eV, although energies in the range 10-1000 eV are suitable. The deposition of silicon ad nitrogen was continued until the coating 4 had a thickness of 1000A, although thicknesses of between 500 and 5000A are suitable.

Next chromium atoms 5 were deposited on top of the coating 4, again by electron beam evaporation in vacuum, simultaneously with continued bombardment with nitrogen ions to form an outer layer 6. In this case, however the rates of arrival of the chromium and nitrogen were controlled so as to provide a final composition in which

the chromium: nitrogen ratio was approximately 10:1. The deposition of chromium and nitrogen was continued until the final coating 6 on the substrate 1 was one micron.

The coated substrate 1 was exposed to an oxygen rich atmosphere at a temperature of 600°C for 100 hours. Upon subsequent sectioning and surface analysis by secondary ion mas spectrometry it was found that although a superficial oxidation of the outer layer 6 had occured to a depth of about 4000A, the remainder of the outer layer 6 was metallic chromium. It was found also that the barrier layer 4 of silicon nitride was intact and no penetration of oxygen to the substrate 1 had occurred.

In a service application such as a compressor blade for a gas turbine aero engine, the oxidation - preventing coating 6 needs to be protected against the erosive effects of particulate matter in the air stream passing through the engine. This is best done by providing a third, sacrificial, layer made of a material which is tough, inert and preferably able to protect the substrate against the in-diffusion of hydrogen.

Suitable materials for this purpose are the noble metals with ruthenium being preferred and platinum being the next most favoured material. Noble metals are particularly suitable because, as they do not oxidise, they retain their metallic natural toughness and ductility. As a result, the impact energy of particulate matter will be absorbed by plastic deformation rather than by brittle fracture and subsequent loss. Also, their catalytic activities, particularly so in the case of ruthenium, in causing the recombination of atomic hydrogen to molecular hydrogen and subsequent release from the surface of the noble metal, is made use of. In practice, the surface concentration of hydrogen is found to be reduced by a

factor of 10 compared with that of a specimen of similar uncoated titanium alloy. Again, the protective coating can be formed by an ion-assisted coating technique, preferably to a thickness of between 2 and 5 microns, using argon ions with energies between 100 and 500 eV.

Claims

1. An artefact made of titanium or a titanium alloy having upon a surface a protective coating comprising an outer layer which is such as not to react with a reactive environment against which the artefact is to be protected or to form as passivating compound therewith and an inner barrier layer such as to prevent interdiffusion between the outer layer and the artefact.

2. An artefact according to claim 1 wherein the outer layer of the protective coating is made of chromium; chromium/nitrogen; nickel 20% chromium alloy; silicon oxide; silicon or boron.

3. An artefact according to claim 2 wherein the inner barrier layer is made of silicon nitride.

4. An artefact according to claim 3 wherein the outer layer consists of chromium and nitrogen in proportions of approximately 10:1.

5. An artefact according to any of the claims 1 to 4 wherein the protective coating includes an outermost layer adapted to prevent erosion of the outer layer of the protective coating.

6. An artefact according to claim 5 wherein the outermost layer is adapted to prevent the inward diffusion of hydrogen from the gaseous environment.

7. An artefact according to claim 6 wherein the outermost layer of the protective coating is made of a noble metal.

8. An artefact according to claim 7 wherein the outermost layer of the protective coating is made of ruthenium or platinum.

9. A method of protecting artefacts made of titanium or its alloys against the effects of a reactive gaseous environment, comprising the operation of forming upon the artefact to be protected a protective coating including an outer layer made of a material which either does not react with the gaseous environment or forms a passivating compound there with and an inner barrier layer such as to prevent interdiffusion between the outer layer and the artefact.

10. A method according to claim 9 wherein the outer layer of the protective coating is made of chromium; chromium/nitrogen; nickel 20% chromium alloy; silicon oxide; silicon or boron.

11. A method according to claim 10 wherein the inner barrier layer is made of silicon nitride.

12. A method according to claim 11 including the operations of depositing by a vacuum deposition process silicon and nitrogen together at rates such that Si_3N_4 is formed and subsequently depositing by a vacuum depostion process chromium and nitrogen at rates such as to provide an outer layer consisting of chromium and nitrogen in proportions of approximately 10:1 respectively.

13. A method according to claim 12 wherein the vacuum deposition process is a combination of electron beam evaporation and ion bombardment.

14. A method according to claim 13 wherein the nitrogen ions have an energy in the range 10-1000 eV, the deposition is continued until the ineer layer has a thickness in the range 500A to 5000A and the deposition of the outer layer is continued until the total thickness of the protective coating is approximately 1 micron.

15. A method according to any proceding claim wherein there is included the operation of depositing an outermost layer adapted to prevent erosion of the outer layer of the protective coating.

16. A method according to claim 15 wherein the outermost layer is made of a material which is able to protect the titanium artefact against the inward diffusion of hydrogen from the gaseous environment.

17. A method according the claim 16 wherein the outermost layer is made of a noble metal.

18. A method according to claim 17 wherein the noble metal is ruthenium or platinum.

19. An artefact made of titanium or an alloy of titanium having upon a surface a protective coating substantially as hereinbefore described and with reference to the accompanying drawing.

20. A method for protecting an artefact made of titanium or a titanium alloy against the effects of a reactive gaseous environment substantially as hereinbefore described and with reference to the accompanying drawing.

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